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"Molecular Filtration in Nanotubule Membranes: Sorting Molecules on the Basis of Size and Chemistry"

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CHAPTER TWELVE

MOLECULAR FILTRATION IN NANOTUBULE MEMBRANES: SORTING MOLECULES ON THE BASIS OF SIZE AND CHEMISTRY

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Abstract

Membrane-based chemical separations constitute an emerging field of research. This is because membrane-based separations are potentially less energy-intensive and more cost-effective than competing separation methods. Polymeric membranes that contain a collection of monodisperse gold nanotubules with molecular dimensions were used to filter molecules based on their difference in size. Also, we will discuss how these tubules can be modified with thiols to separate molecules based on differences in their chemical properties.

Introduction

Chemical separations are a major cost and labor component of most chemical, pharmaceutical, and petrochemical processes. Examples of such separations include distillation, cryogenics, chromatography, and separation processes based on membranes. Some examples of membrane-based separations are filtration, water purification using reverse osmosis, gas separations, and electrochemical processes such as chlor-alkali production. Membrane-based separations such as these are becoming increasingly important in the industrial realm. Additionally, membranes have a broad future in large scale industrial gas and liquid-liquid separations. In this report we discuss the preparation of a new class of separation membranes, one that contains nanoscopic tubules of molecular dimensions and can therefore separate molecules on the basis of size. Furthermore, the chemistry of these tubules can be manipulated by adsorbing thiols with different terminal groups. This will give rise to chemical transport selectivity.

Sized-Based Separations

Our group has in recent years been exploring a process we call "template synthesis." This process entails synthesizing the desired material within the pores of a porous membrane or other solid. This is an extremely general process, adaptable to almost any synthetic method. We have used this process to prepare a large variety of nanomaterials including polymers, metals, semiconductors, carbons, and Li-intercalation materials.[2-6] We have also used this approach to prepare various kinds of composites.[7] For preparation of the molecular-filtration

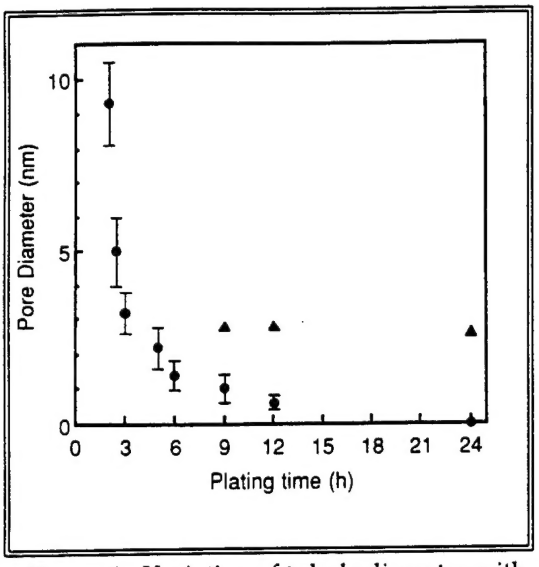

Figure 1. Variation of tubule diameter with plating time. Adapted from Ref. 8 with permission from Elsevier Science.

membranes, we used porous track-etched polycarbonate membranes (pore diameter 30 nm) as templates and plated the membranes with gold to make tubules with inside diameters of molecular dimensions.

The electroless gold deposition procedure used to plate the polycarbonate membranes has been previously described.[3,8] In this method, a catalyst is applied to the surfaces of the membrane, including the pore walls, which catalyzes the reduction of the gold ion from solution. Using the electroless deposition method, the inside diameter of the gold tubules produced can be varied by varying the plating time. The tubule diameter can be varied from 30 nm (pore size of the unplated polycarbonate membranes), to <1 nm depending on how long the membrane is left in the plating solution.

The diameter of the nanotubules can be determined using gas permeation measurements. The steady state gas flux can be related to the diameter of the nanotubules, provided the thickness of the membrane, and the number of pores are known.[8] Figure 1 shows the variation of the tubule diameter with plating time. The tubule diameter can be as small as 1 nm (i.e., of a molecular dimension). This allows for new possibilities—separating molecules based on their size differences.[9] Thus, in a solution containing a mixture of small and large molecules, the membrane will allow transport the smaller molecule but block transport of the larger molecule. We will examine this in detail with four different molecular pairs.

The first pair of molecules we used for sized-based separations was methylviologen chloride, (MV^{2+})/ ruthenium tris(2,2′ bipyridine) chloride, ($Ru(bpy)_3^{2+}$). The MV^{2+} is the small molecule, with a diameter of ~4 Å,

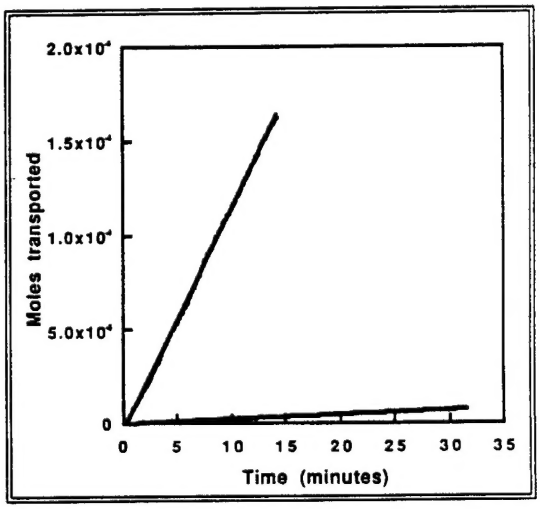

Figure 2. Flux of MV^{2+} and $Ru(bpy)_3^{2+}$ in gold nanotubular membrane with pore diameter of 5.5 nm. Adapted with permission from Ref. 9. Copyright 1997 American Association for the Advancement of Science.

while the diameter of the $Ru(bpy)_3^{2+}$ is ~10 Å. We will first discuss simpler single molecule permeation experiments, which involve measuring the flux of first one molecule, then the other, across the same membrane. As seen in Figure 2, the ratio of molecular fluxes in the largest nanotubule diameter (5.5 nm) is 55. This is substantially larger than the ratio of the diffusion coefficients of these two molecules, which is 1.5, and thus the membrane shows molecular sieving. This sieving effect can be increased by decreasing the tubule diameter. The flux ratio increases to 88 and 172 for tubule diameters 3.2 nm and 2.0 nm, respectively. When the tubule diameter is 0.6 nm there is no measurable flux of $Ru(bpy)_3^{2+}$ but there is a finite flux for MV^{2+}. The selectivity coefficient for this membrane is therefore infinity, and this demonstrates that we can filter molecules based on size.

While examining the flux of the two molecules individually is instructive, the more realistic (and more difficult) experiment is to have both molecules in solution together. Figure 3a shows the UV-spectrum of equimolar concentrations of these two molecules. As can be seen, $Ru(bpy_3^{2+})$ has a stronger absorbance than MV^{2+}. Figure 3b shows the permeate from a dual molecule experiment after 72 hours of permeation time. Within our ability to measure, there is no $Ru(bpy)_3^{2+}$ in the permeate even after three days. Thus, to our ability to make the measurement, we have filtered the two molecules on the basis of molecular size.

Other pairs we have examined include pyridine/quinine, anilinium chloride/rhodamine B, and phenol/bromocresolgreen. We will discuss these results below.

Figure 4a shows the UV spectrum of a solution that is 0.5 mM in both pyridine and quinine. It is important to note that pyridine has a lower absorbance than quinine. Figure 4b shows the permeate after a 72 hours of permeation experiment. There is no evidence for the presence of quinine. Within the detection limit for the larger molecule, we have again filtered these two molecules on the basis of molecular

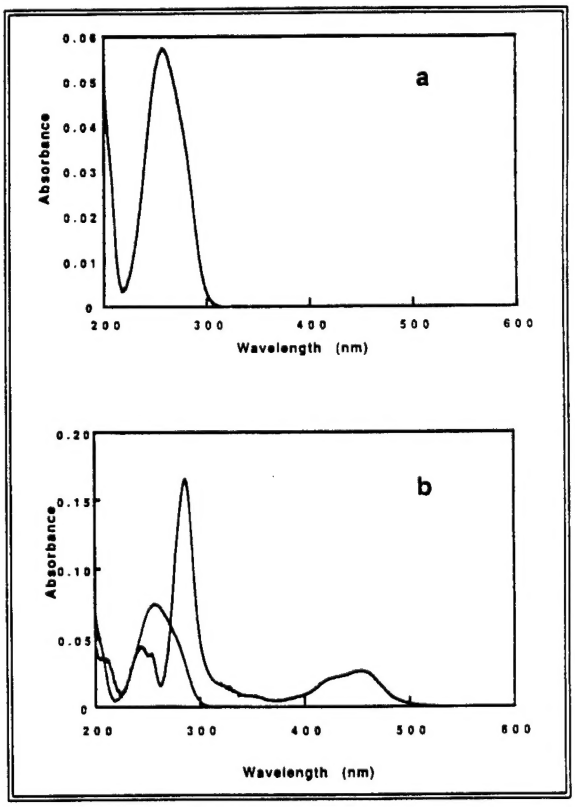

Figure 3. a) UV spectrum of equimolar concentrations of MV^{2+} and $Ru)bpy)_3^{2+}$; **b)** UV spectrum of the permeate after 72 hours.

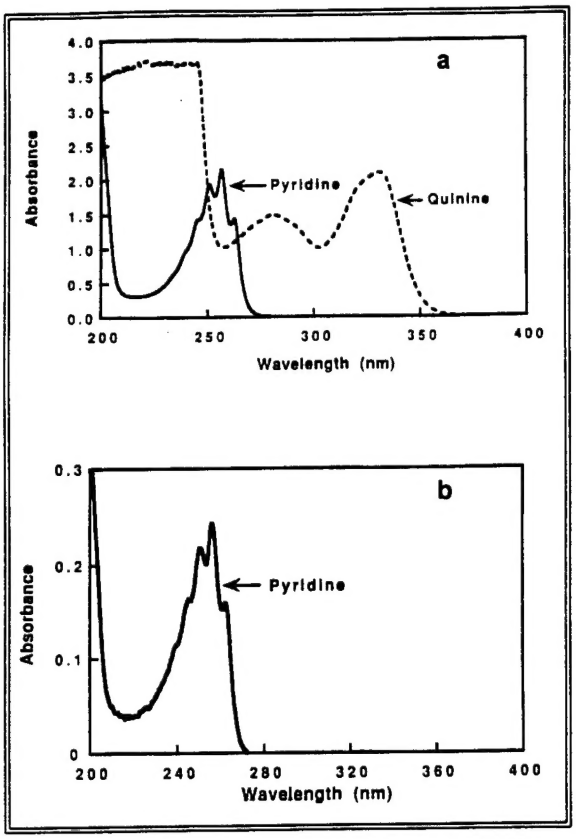

Figure 4. **a)** UV spectrum of 0.5 mM pyridine and quinine; **b)** UV spectrum of the permeate after 72 hours. Adapted with permission from Ref. 9. Copyright 1997 American Association for the Advancement of Science.

size.

The molecular filtration of two monovalent cations, anilinium chloride/rhodamine B was also studied. Rhodamine has large absorbance compared to aniline. After eight days, the permeate shows no evidence of rhodamine B, the bigger molecule.

The final pair studied was bromocresol green (BCG)/phenol. Again, the advantage is that BCG shows larger absorbance than phenol, such that smaller amounts of BCG than phenol can be detected. After a one-day permeation experiment, no BCG could be detected in the permeate solution.

Small molecule	Large molecule	Minimal Selectivity Coefficients
Methylviologen chloride	Ruthenium tris(2,2'-bipyridine) chloride	1500
Pyridine	Quinine	15000
Anilinium chloride	Rhodamine B	130000

Table 1.

In all the above examples, we were unable to detect the presence of the larger molecule. We used the data from these experiments to calculate a minimal selectivity coefficient, α_{min}. This was obtained by dividing the concentration of the smaller molecule (obtained from the UV absorbance) by the detection limit of the larger molecule. The minimal selectivity coefficient for the anilinium chloride/rhodamine pair was 130,000. Table 1 shows the minimal selectivity coefficients for the four molecular pairs. It is again important to emphasize that in all cases the big molecule could not be detected in the permeation solution. Hence, the real selectivity coefficients are larger, indeed, perhaps infinite.

Chemical Transport Selectivity

We have shown that the gold nanotubular membranes can show ion-permselectivity[1] and size-based selectivity.[9] We finally looked at possibility of using chemical interactions (e.g., hydrophobic, hydrogen-bonding) between the membrane material and the molecule to control transport selectivity. This is done by self-assembling thiols with different terminal groups onto the gold

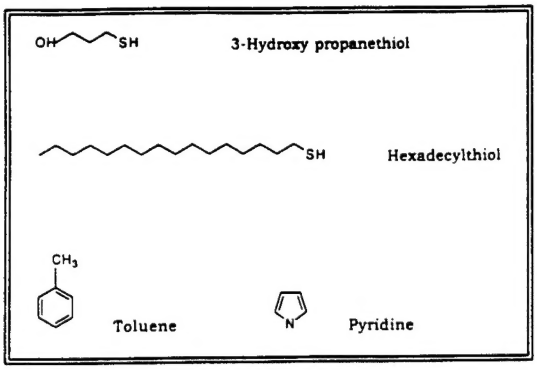

Figure 5. The thiols and the two molecules used for the study.

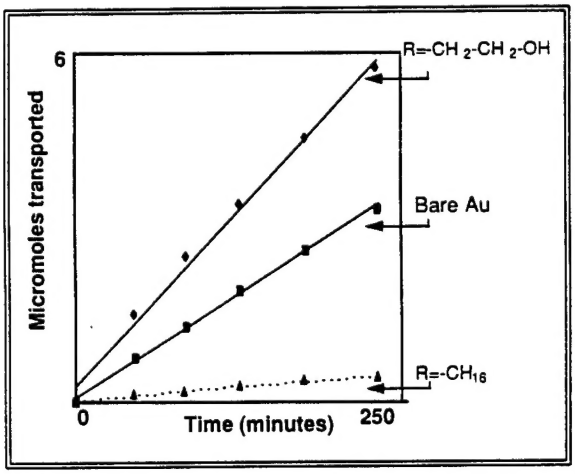

Figure 6. Flux of pyridine in bare gold, -C_{16}- and -CH_2CH_2OH-terminated thiol membranes.

tubules. The two thiols used in this study were hexadecyl thiol (-C_{16}, hydrophobic) and 3-hydroxypropanethiol (-CH_2CH_2-OH, hydrophilic), and the molecular pair was pyridine/toluene (Figure 5). Figure 6 shows the flux of pyridine in C_{16}, OH-terminated, and bare gold membranes. When the nanotubule diameter is large (20 nm), the ratio of pyridine in the -CH_2CH_2-OH vs. -C_{16} is only 1.4. This ratio increased when smaller nanotubules were used. The ratio is increased to 6 and 25 with nanotubules of diameter 2 nm and 1 nm, respectively.

This selectivity can be attributed to the extraction of the pyridine into the -CH_2CH_2-OH- vs. -C_{16}-terminated membranes. The argument can be made that the tubule diameters are smaller when a -C_{16} thiol is used as opposed to -CH_2CH_2-OH thiol. To examine whether this difference in tubule diameter is the cause of the selectivity, we looked at the flux of a hydrophobic molecule, toluene, in the same membranes. Toluene has a higher flux in the -C_{16} than in the -CH_2CH_2-OH thiol membrane, which shows that chemistry, not size, is the basis of the selectivity.

In conclusion, we have shown that nanotubular membranes can have both size-based and chemical-based selectivity. In previous work, we have shown that the same membranes can have charge-based selectivity.[1] Perhaps we now have all the basic ingredients to mimic nature's highly selective chemical transport systems.

Acknowledgments

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